

Title: LUBRICANTS HAVING AN OVERBASED METAL SALTS AND ORGANIC PHOSPHITES

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Cross Reference to Related Application

This application claims priority from provisional application Serial No. 60/106,877, filed November 3, 1998, the entire disclosure of which is hereby incorporated by reference.

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Technical Field of the Invention

This invention relates to lubricants and especially for those lubricants which are used in manual transmissions. More specifically, the lubricant comprises (A) at least one basic metal salt of an acidic organic compound and (B) at least one hydrocarbyl phosphite.

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Background of the Invention

Manual transmissions are common for off road and heavy duty vehicles. The manual transmission lubricants must provide protection to the components of the transmission as well as desirable shift characteristics for the driver. Many off road and heavy duty manual transmissions are non-synchronized transmissions. These transmission rely on composite friction plates and steel plates to provide shifting. These plates must slid over each other during the shifting process. The lubricants must provide the needed friction properties as well as protecting against plate wear.

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Manual transmission fluids, with synchronizers, require friction retention to avoid a phenomenon known as synchronizer clashing (sometimes referred to as crashing). Clashing of the synchronizer results when the dynamic co-efficient of friction building between the engaging synchronizer parts (plate to plate or ring to cone) falls below a critical minimum value. Below this critical minimum value the synchronizer parts do not attain zero relative velocity and the lockup mechanism (e.g., spline camphers)

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contacts the rotating member (e.g., cone camphers) resulting in a loud noise (clashing/crashing).

Thermal stability is the ability of the fluid to withstand high operating temperatures without the formation of degradation or breakdown products from the fluid's components. For lubricants, especially manual transmission fluids, to be effective they must provide thermal stability. Additionally, the lubricants must have sufficient durability. Durability is a measure of the lubricants ability to provide antiwear and extreme pressure protection needed for transmission in gears. For manual transmissions, one measure of durability is the Mack T2180 High Temperature Cycle Test.

It is desirable to have a fluid which provides the friction qualities for the manual transmission while also providing thermal stability.

Summary of the Invention

This invention relates to a lubricant comprising (A) a basic metal salt of an acidic organic compound and (B) a hydrocarbyl phosphite, provided that the lubricant is free of metal deactivators. In one aspect the lubricant is a manual transmission fluid. The lubricants provide good friction, good antiwear and thermal stability properties.

Detailed Description of the Preferred Embodiments

The term "hydrocarbyl" includes hydrocarbon, as well as substantially hydrocarbon, groups. Substantially hydrocarbon describes groups which contain non-hydrocarbon substituents which do not alter the predominately hydrocarbon nature of the group.

Examples of hydrocarbyl groups include the following:

(1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, aromatic-, aliphatic- and alicyclic-substituted aromatic substituents and the like as well as cyclic substituents wherein the ring is completed through another portion of the molecule (that is, for example, any

two indicated substituents may together form an alicyclic radical);

(2) substituted hydrocarbon substituents, that is, those substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon substituent; those skilled in the art will be aware of such groups (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.);

(3) hetero substituents, that is, substituents which will, while having a predominantly hydrocarbon character within the context of this invention, contain other than carbon present in a ring or chain otherwise composed of carbon atoms. Suitable heteroatoms will be apparent to those of ordinary skill in the art and include, for example, sulfur, oxygen, nitrogen and such substituents as, e.g., pyridyl, furyl, thienyl, imidazolyl, etc. In general, no more than about 2, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group. Typically, there will be no such non-hydrocarbon substituents in the hydrocarbyl group. Therefore, the hydrocarbyl group is purely hydrocarbon.

The lubricating compositions are free of metal deactivators. Metal deactivators reduce the corrosion of metals, such as copper. Metal deactivators are also referred to as metal passivators. Metal deactivators are typically nitrogen and/or sulfur containing heterocyclic compounds, such as dimercaptotriazoles, triazoles, amino-mercaptotriazoles, imidazoles, thiazoles, tetrazoles, hydroxyquinolines, oxazolines, imidazolines, thiophenes, indoles, indazoles, quinolines, benzoxazines, dithiols, oxazoles, oxatriazoles, pyridines, piperazines, triazines, and derivatives of any one or more thereof.

(A) Basic Metal Salts

The lubricating compositions of the present invention contain (A) at least one basic metal salt of an acidic organic compound. These salts are generally referred to as overbased materials or overbased metal salts. Overbased materials are single phase, homogeneous Newtonian systems characterized by a metal content in excess of that which would be present according to the stoichiometry of the metal and the

particular acidic organic compound reacted with the metal. The basic metal salt is present in an amount up to about 3% by weight. Generally the lubricants contains from about 0.02% to about 5%, or from about 0.05% to about 2%, or from about 0.1% to about 1%. Here and elsewhere in the specification and claims, the range and ratio limits may be combined.

The amount of excess metal is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5. The basic salts of the present invention have a metal ratio of about 1.5, more preferably about 3, more preferably about 7, up to about 40, preferably about 25, more preferably about 20.

The basicity of the overbased materials generally is expressed in terms of a total base number. A total base number is the amount of acid (perchloric or hydrochloric) needed to neutralize all of the overbased material's basicity. The amount of acid is expressed as potassium hydroxide equivalents. Total base number is determined by titration of one gram of overbased material with 0.1 Normal hydrochloric acid solution using bromophenolblue as an indicator. The overbased materials of the present invention generally have a total base number from about 50 to about 1200, or from about 100 to about 1000, or from about 250 to about 900, or from about 500 to about 800.

In one embodiment, the inventors have discovered that when the ratio of the equivalents of overbased material based on total base number to the equivalents of hydrocarbyl phosphite based on phosphorus atoms is at least one the lubricants have improved thermal stability. The equivalents of overbased material is determined by the following equation: $\text{equivalent weight} = (56,100/\text{total base number})$. For instance, an overbased material with a total base number of 200 has an equivalent weight of 280.5 ($\text{eqwt} = 56100/200$). The equivalents of phosphite are determined by dividing the molecular weight of the phosphite by the number of phosphorus atoms in the

phosphite.

The overbased materials (A) are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, preferably carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (mineral oil, naphtha, toluene, xylene, etc.) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter.

The acidic organic compounds useful in making the overbased compositions of the present invention include carboxylic acids, sulfonic acids, phosphorus-containing acids, phenols or mixtures of two or more thereof. Preferably, the acidic organic compounds are carboxylic acids or sulfonic acids with sulfonic and salicylic acids more preferred. Throughout this specification and in the appended claims, any reference to acids, such as carboxylic, or sulfonic acids, is intended to include the acid-producing derivatives thereof such as anhydrides, lower alkyl esters, acyl halides, lactones and mixtures thereof unless otherwise specifically stated.

The carboxylic acids useful in making the overbased salts (A) of the invention may be aliphatic or aromatic, mono- or polycarboxylic acid or acid-producing compounds. These carboxylic acids include lower molecular weight carboxylic acids (e.g., carboxylic acids having up to about 22 carbon atoms such as acids having about 4 to about 22 carbon atoms or tetrapropenyl-substituted succinic anhydride) as well as higher molecular weight carboxylic acids.

The carboxylic acids are preferably oil-soluble. Usually, in order to provide the desired oil-solubility, the number of carbon atoms in the carboxylic acid should be at least about 8, more preferably at least about 18, more preferably at least about 30, more preferably at least about 50. Generally, these carboxylic acids do not contain more than about 400 carbon atoms per molecule.

The lower molecular weight monocarboxylic acids contemplated for use in this invention include saturated and unsaturated acids. Examples of such useful acids include dodecanoic acid, decanoic acid, oleic acid, stearic acid, linoleic acid, tall oil acid, etc. Mixtures of two or more such agents can also be used. An extensive

discussion of these acids is found in Kirk- Othmer "Encyclopedia of Chemical Technology" Third Edition, 1978, John Wiley & Sons New York, pp. 814-871; these pages being incorporated herein by reference.

5 The monocarboxylic acids include isoaliphatic acids. Such acids often contain a principal chain having from about 14 to about 20 saturated, aliphatic carbon atoms and at least one but usually no more than about four pendant acyclic lower alkyl groups. Specific examples of such isoaliphatic acids include 10-methyl-tetradecanoic acid, 3-ethyl-hexadecanoic acid, and 8-methyl-octadecanoic acid. The isoaliphatic acids include mixtures of branch-chain acids prepared by the isomerization of commercial fatty acids (oleic, linoleic or tall oil acids) of, for example, about 16 to about 10 20 carbon atoms.

High molecular weight carboxylic acids may also be used in the present invention. These acids have a substituent group derived from a polyalkene. The polyalkene is characterized as containing at least about 30 carbon atoms, preferably at least about 35, more preferably at least about 50, and up to about 300 carbon atoms, preferably about 200, more preferably about 150. In one embodiment, the polyalkene is characterized by an Mn (number average molecular weight) value of at least about 500, generally about 500 to about 5000, preferably about 800 to about 2500. In another embodiment, Mn varies between about 500 to about 1200 or 1300.

20 The polyalkenes include homopolymers and interpolymers of polymerizable olefin monomers of 2 to about 16 carbon atoms. The olefins may be monoolefins such as ethylene, propylene, 1-butene, isobutene, and 1-octene; or a polyolefinic monomer, preferably diolefinic, monomer such 1,3-butadiene and isoprene. Preferably the monomers contain from 2 to about 6 carbon atoms, more preferably 2 to about 4, 25 more preferably 4. The interpolymers include copolymers, terpolymers, tetrapolymers and the like. Preferably, the interpolymer is a homopolymer. An example of a preferred homopolymer is a polybutene, preferably a polybutene in which about 50% of the polymer is derived from isobutylene. The polyalkenes are prepared by conventional procedures.

In one embodiment, the polyalkene is characterized as containing from about 8 up to about 300, or from about 30 up to about 200, or from about 35 up to about 100 carbon atoms. In one embodiment, the polyalkene is characterized by an n (number average molecular weight) of at least about 400 or at least about 500. Generally, the polyalkene is characterized by having an n from about 500 up to about 5000, or from about 700 up to about 3000, or from about 800 up to 2500, or from about 900 up to about 2000. In another embodiment, M_n varies from about 500 up to about 1500, or from about 700 up to about 1300, or from about 800 up to about 1200.

The abbreviation M_n is the conventional symbol representing number average molecular weight. Gel permeation chromatography (GPC) is a method which provides both weight average and number average molecular weights as well as the entire molecular weight distribution of the polymers. For purpose of this invention a series of fractionated polymers of isobutene, polyisobutene, is used as the calibration standard in the GPC. The techniques for determining M_n and M_w values of polymers are well known and are described in numerous books and articles. For example, methods for the determination of n and molecular weight distribution of polymers is described in W.W. Yan, J.J. Kirkland and D.D. Bly, "Modern Size Exclusion Liquid Chromatographs", J. Wiley & Sons, Inc., 1979.

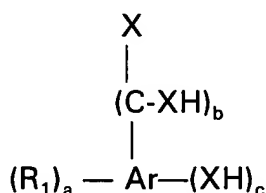
The higher molecular weight mono- and polycarboxylic acids suitable for use in making the overbased salts (A) are well known in the art and have been described in detail, for example, in the following U.S., British and Canadian patents: U.S. Patents 3,024,237; 3,172,892; 3,219,666; 3,245,910; 3,271,310; 3,272,746; 3,278,550; 3,306,907; 3,312,619; 3,341,542; 3,367,943; 3,374,174; 3,381,022; 3,454,607; 3,470,098; 3,630,902; 3,755,169; 3,912,764; and 4,368,133; British Patents 944,136; 1,085,903; 1,162,436; and 1,440,219; and Canadian Patent 956,397. These patents are incorporated herein by reference for their disclosure of higher molecular weight mono- and polycarboxylic acids and methods for making the same.

Illustrative carboxylic acids include palmitic acid, stearic acid, myristic acid, oleic

acid, linoleic acid, behenic acid, hexatriacontanoic acid, tetrapropylenyl-substituted glutaric acid, polybutenyl-substituted succinic acid derived from a polybutene ($M_n = 200-1500$, preferably $300-1000$), polypropenyl-substituted succinic acid derived from a polypropene, ($M_n = 200-1000$, preferably $300-900$), octadecyl-substituted adipic acid, chlorostearic acid, 9-methylstearic acid, dichlorostearic acid, stearyl-benzoic acid, eicosanyl-substituted naphthoic acid, dilauryl-decahydronaphthalene carboxylic acid, mixtures of any of these acids, their alkali and alkaline earth metal salts, and/or their anhydrides. A preferred group of aliphatic carboxylic acids includes the saturated and unsaturated higher fatty acids containing from about 12 to about 30 carbon atoms. Illustrative of these acids are lauric acid, palmitic acid, oleic acid, linoleic acid, linolenic acid, oleostearic acid, stearic acid, myristic acid, and undecalinic acid, alpha-chlorostearic acid, and alphanitrolauric acid.

In another embodiment, the carboxylic acid is an alkylalkyleneglycol-acetic acid, more preferably alkylpolyethyleneglycol-acetic acid. Some specific examples of these compounds include: iso-stearyl-pentaethyleneglycol-acetic acid; iso-stearyl-O-($\text{CH}_2\text{CH}_2\text{O}$)₅CH₂CO₂Na; lauryl-O-($\text{CH}_2\text{CH}_2\text{O}$)_{2.5}-CH₂CO₂H; lauryl-O-($\text{CH}_2\text{CH}_2\text{O}$)_{3.3}CH₂CO₂H; oleyl-O-($\text{CH}_2\text{CH}_2\text{O}$)₄-CH₂CO₂H; lauryl-O-($\text{CH}_2\text{CH}_2\text{O}$)_{4.5}CH₂CO₂H; lauryl-O-($\text{CH}_2\text{CH}_2\text{O}$)₁₀CH₂CO₂H; lauryl-O-($\text{CH}_2\text{CH}_2\text{O}$)₁₆CH₂CO₂H; octyl-phenyl-O-($\text{CH}_2\text{CH}_2\text{O}$)₈CH₂CO₂H; octyl-phenyl-O-($\text{CH}_2\text{CH}_2\text{O}$)₁₉CH₂CO₂H; 2-octyl-decanyl-O-($\text{CH}_2\text{CH}_2\text{O}$)₆CH₂CO₂H. These acids are available commercially from Sandoz Chemical under the tradename Sandopan acids.

In another embodiment, the carboxylic acids are aromatic carboxylic acids. A group of useful aromatic carboxylic acids are those of the formula



wherein R_1 is an aliphatic hydrocarbonyl group of preferably about 4 to about 400 carbon

atoms, a is a number in the range of zero to about 4, usually 1 or 2, Ar is an aromatic group, each X is independently sulfur or oxygen, preferably oxygen, b is a number in the range of from 1 to about 4, usually 1 or 2, c is a number in the range of zero to about 4, usually 1 to 2, with the proviso that the sum of a, b and c does not exceed the number of valences of Ar. Preferably, R₁ and a are such that there is an average of at least about 8 aliphatic carbon atoms provided by the R₁ groups. Examples of aromatic carboxylic acids include substituted and non-substituted benzoic, phthalic and salicylic acids or anhydrides.

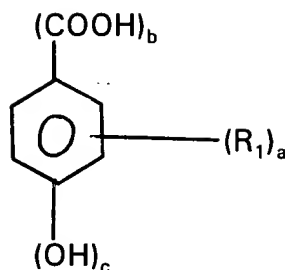
The R₁ group is a hydrocarbonyl group that is directly bonded to the aromatic group Ar. R₁ preferably contains about 6 to about 80 carbon atoms, preferably about 6 to about 30 carbon atoms, more preferably about 8 to about 25 carbon atoms, and advantageously about 8 to about 15 carbon atoms. R₁ groups may be derived from one or more of the above-described polyalkenes. Examples of R₁ groups include butyl, isobutyl, pentyl, octyl, nonyl, dodecyl, 5-chlorohexyl, 4-ethoxypentyl, 3-cyclohexyloctyl, 2,3,5-trimethylheptyl, and substituents derived from polymerized olefins such as polyethylenes, polypropylenes, polyisobutylenes, ethylene-propylene copolymers, chlorinated olefin polymers, oxidized ethylene-propylene copolymers, propylene tetramer and tri(isobutene).

Examples of the R₁ groups include butyl, isobutyl, pentyl, octyl, nonyl, dodecyl, and substituents derived from the above-described polyalkenes such as polyethylenes, polypropylenes, polyisobutylenes, ethylene-propylene copolymers, oxidized ethylene-propylene copolymers, and the like.

The aromatic group Ar may have the same structure as any of the aromatic groups Ar discussed below. Examples of the aromatic groups that are useful herein include the polyvalent aromatic groups derived from benzene, naphthalene, anthracene, etc., preferably benzene. Specific examples of Ar groups include phenylenes and naphthylene, e.g., methylphenylenes, ethoxyphenylenes, isopropylphenylenes, hydroxyphenylenes, dipropoxynaphthylenes, etc.

Within this group of aromatic acids, a useful class of carboxylic acids are those

of the formula



wherein R_1 is defined above, a is a number in the range of from zero to about 4, preferably 1 to about 2; b is a number in the range of 1 to about 4, preferably 1 to about 2, c is a number in the range of zero to about 4, preferably 1 to about 2, and more preferably 1; with the proviso that the sum of a , b and c does not exceed 6. Preferably, R_1 and a are such that the acid molecules contain at least an average of about 12 aliphatic carbon atoms in the aliphatic hydrocarbon substituents per acid molecule. Preferably, b and c are each one and the carboxylic acid is a salicylic acid.

The salicylic acids can be aliphatic hydrocarbon-substituted salicyclic acids wherein each aliphatic hydrocarbon substituent contains an average of at least about 8 carbon atoms per substituent and 1 to 3 substituents per molecule. Overbased salts prepared from such salicyclic acids wherein the aliphatic hydrocarbon substituents are derived from the above-described polyalkenes, particularly polymerized lower 1-mono-olefins such as polyethylene, polypropylene, polyisobutylene, ethylene/propylene copolymers and the like and having average carbon contents of about 30 to about 400 carbon atoms are particularly useful.

The above aromatic carboxylic acids are well known or can be prepared according to procedures known in the art. Carboxylic acids of the type illustrated by these formulae and processes for preparing their neutral and basic metal salts are well known and disclosed, for example, in U.S. Patents 2,197,832; 2,197,835; 2,252,662; 2,252,664; 2,714,092; 3,410,798; and 3,595,791.

The sulfonic acids useful in making the overbased salts (A) of the invention

include the sulfonic and thiosulfonic acids. Generally they are salts of sulfonic acids. The sulfonic acids include the mono- or polynuclear aromatic or cycloaliphatic compounds. The oil-soluble sulfonates can be represented for the most part by one of the following formulae: $R_2-T-(SO_3)_a$ and $R_3-(SO_3)_b$, wherein T is a cyclic nucleus such as, for example, benzene, naphthalene, anthracene, diphenylene oxide, diphenylene sulfide, petroleum naphthenes, etc.; R_2 is an aliphatic group such as alkyl, alkenyl, alkoxy, alkoxyalkyl, etc.; $(R_2) + T$ contains a total of at least about 15 carbon atoms; and R_3 is an aliphatic hydrocarbyl group containing at least about 15 carbon atoms. Examples of R_3 are alkyl, alkenyl, alkoxyalkyl, carboalkoxyalkyl, etc. Specific examples of R_3 are groups derived from petrolatum, saturated and unsaturated paraffin wax, and the above-described polyalkenes. The groups T, R_2 , and R_3 in the above Formulae can also contain other inorganic or organic substituents in addition to those enumerated above such as, for example, hydroxy, mercapto, halogen, nitro, amino, nitroso, sulfide, disulfide, etc. In the above Formulae, a and b are at least 1. In one embodiment, the sulfonic acids have a substituent (R_2 or R_3) which is derived from one of the above-described polyalkenes.

Illustrative examples of these sulfonic acids include monoeicosanyl-substituted naphthalene sulfonic acids, dodecylbenzene sulfonic acids, didodecylbenzene sulfonic acids, dinonylbenzene sulfonic acids, cetylchlorobenzene sulfonic acids, dilauryl beta-naphthalene sulfonic acids, the sulfonic acid derived by the treatment of polybutene having a number average molecular weight (M_n) in the range of 500 to 5000, preferably 800 to 2000, more preferably about 1500 with chlorosulfonic acid, nitronaphthalene sulfonic acid, paraffin wax sulfonic acid, cetyl-cyclopentane, sulfonic acid, lauryl-cyclohexane sulfonic acids, polyethylenyl-substituted sulfonic acids derived from polyethylene ($M_n = 300-1000$, preferably 750), etc. Normally the aliphatic groups will be alkyl and/or alkenyl groups such that the total number of aliphatic carbons is at least about 8, preferably at least 12 up to about 400 carbon atoms, preferably about 250.

Another group of sulfonic acids are mono-, di-, and tri-alkylated benzene and

naphthalene (including hydrogenated forms thereof) sulfonic acids. Illustrative of synthetically produced alkylated benzene and naphthalene sulfonic acids are those containing alkyl substituents having from about 8 to about 30 carbon atoms, preferably about 12 to about 30 carbon atoms, and advantageously about 24 carbon atoms. Such acids include di-isododecyl-benzene sulfonic acid, polybutenyl-substituted sulfonic acid, polypropylenyl-substituted sulfonic acids derived from polypropene having an $M_n = 300-1000$, preferably 500-700, cetylchlorobenzene sulfonic acid, dicetylnaphthalene sulfonic acid, di-lauryldiphenylether sulfonic acid, diisononylbenzene sulfonic acid, di-isooctadecylbenzene sulfonic acid, stearyl naphthalene sulfonic acid, and the like.

Specific examples of oil-soluble sulfonic acids are mahogany sulfonic acids; bright stock sulfonic acids; sulfonic acids derived from lubricating oil fractions having a Saybolt viscosity from about 100 seconds at 100°F to about 200 seconds at 210°F; petrolatum sulfonic acids; mono- and poly-wax-substituted sulfonic and polysulfonic acids of, e.g., benzene, naphthalene, phenol, diphenyl ether, naphthalene disulfide, etc.; other substituted sulfonic acids such as alkyl benzene sulfonic acids (where the alkyl group has at least 8 carbons), cetylphenol mono-sulfide sulfonic acids, dilauryl beta naphthyl sulfonic acids, and alkaryl sulfonic acids such as dodecyl benzene "bottoms" sulfonic acids.

Dodecyl benzene "bottoms" sulfonic acids are the material leftover after the removal of dodecyl benzene sulfonic acids that are used for household detergents. These materials are generally alkylated with higher oligomers. The bottoms may be straight-chain or branched-chain alkylates with a straight-chain dialkylate preferred.

The production of sulfonates from detergent manufactured by-products by reaction with, e.g., SO_3 , is well known to those skilled in the art. See, for example, the article "Sulfonates" in Kirk-Othmer "Encyclopedia of Chemical Technology", Second Edition, Vol. 19, pp. 291 et seq. published by John Wiley & Sons, N.Y. (1969).

The phosphorus-containing acids useful in making the basic metal salts (A) of the present invention include any phosphorus acids such as phosphoric acid or esters; and thiophosphorus acids or esters, including mono and dithiophosphorus acids or esters. Preferably, the phosphorus acids or esters contain at least one, preferably two, hydrocarbyl groups containing from 1 to about 50 carbon atoms, typically 1 to about 30, preferably 3 to about 18, more preferably about 4 to about 8.

In one embodiment, the phosphorus-containing acids are dithiophosphoric acids which are readily obtainable by the reaction of phosphorus pentasulfide (P_2S_5) and an alcohol or a phenol. The reaction involves mixing at a temperature of about 20°C to about 200°C four moles of alcohol or a phenol with one mole of phosphorus pentasulfide. Hydrogen sulfide is liberated in this reaction. The oxygen-containing analogs of these acids are conveniently prepared by treating the dithioic acid with water or steam which, in effect, replaces one or both of the sulfur atoms with oxygen.

In another embodiment, the phosphorus-containing acid is the reaction product of the above-described polyalkene and phosphorus sulfide. Useful phosphorus sulfide-containing sources include phosphorus pentasulfide, phosphorus sesquisulfide, phosphorus heptasulfide and the like.

The reaction of the polyalkene and the phosphorus sulfide generally may occur by simply mixing the two at a temperature above 80°C , preferably between 100°C and 300°C . Generally, the products have a phosphorus content from about 0.05% to about 10%, preferably from about 0.1% to about 5%. The relative proportions of the phosphorizing agent to the olefin polymer is generally from 0.1 part to 50 parts of the phosphorizing agent per 100 parts of the olefin polymer.

The phosphorus-containing acids useful in the present invention are described

in U.S. Patent 3,232,883 issued to Le Suer. This reference is herein incorporated by reference for its disclosure to the phosphorus-containing acids and methods for preparing the same.

The phenols useful in making the basic metal salts (A) of the invention can be represented by the formula $(R_1)_a\text{-Ar-(OH)}_b$, wherein R_1 is defined above; Ar is an aromatic group; a and b are independently numbers of at least one, the sum of a and b being in the range of two up to the number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar. Preferably, a and b are independently numbers in the range of 1 to about 4, more preferably 1 to about 2. R_1 and a are preferably such that there is an average of at least about 8 aliphatic carbon atoms provided by the R_1 groups for each phenol compound.

While the term "phenol" is used herein, it is to be understood that this term is not intended to limit the aromatic group of the phenol to benzene. Accordingly, it is to be understood that the aromatic group as represented by "Ar", as well as elsewhere in other formulae in this specification and in the appended claims, can be mononuclear such as a phenyl, a pyridyl, or a thienyl, or polynuclear. The polynuclear groups can be of the fused type wherein an aromatic nucleus is fused at two points to another nucleus such as found in naphthyl, anthranyl, etc. The polynuclear group can also be of the linked type wherein at least two nuclei (either mononuclear or polynuclear) are linked through bridging linkages to each other. These bridging linkages can be chosen from the group consisting of alkylene linkages, ether linkages, keto linkages, sulfide linkages, polysulfide linkages of 2 to about 6 sulfur atoms, etc.

The number of aromatic nuclei, fused, linked or both, in Ar can play a role in determining the integer values of a and b. For example, when Ar contains a single aromatic nucleus, the sum of a and b is from 2 to 6. When Ar contains two aromatic nuclei, the sum of a and b is from 2 to 10. With a tri-nuclear Ar moiety, the sum of a and b is from 2 to 15. The value for the sum of a and b is limited by the fact that it cannot exceed the total number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar.

The metal compounds useful in making the basic metal salts (A) are alkali,

alkaline earth and transition metals. Preferably, any Group I or Group II metal compounds (CAS version of the Periodic Table of the Elements). The Group I metals of the metal compound include alkali metals (sodium, potassium, lithium, etc.) as well as Group IB metals such as copper. The Group I metals are preferably sodium, potassium, lithium and copper, more preferably sodium or potassium, and more preferably sodium. The Group II metals of the metal base include the alkaline earth metals (magnesium, calcium, barium, etc.) as well as the Group IIB metals such as zinc or cadmium. Preferably the Group II metals are magnesium, calcium, or zinc, preferably magnesium or calcium, more preferably magnesium. Generally the metal compounds are delivered as metal salts. The anionic portion of the salt can be hydroxyl, oxide, carbonate, borate, nitrate, etc.

An acidic material is used to accomplish the formation of the basic metal salt (A). The acidic material may be a liquid such as formic acid, acetic acid, nitric acid, sulfuric acid, etc. Acetic acid is particularly useful. Inorganic acidic materials may also be used such as HCl, SO₂, SO₃, CO₂, H₂S, etc, preferably CO₂. A preferred combination of acidic materials is carbon dioxide and acetic acid.

A promoter is a chemical employed to facilitate the incorporation of metal into the basic metal compositions. Among the chemicals useful as promoters are water, ammonium hydroxide, organic acids of up to about 8 carbon atoms, nitric acid, sulfuric acid, hydrochloric acid, metal complexing agents such as alkyl salicylaldehyde, and alkali metal hydroxides such as lithium hydroxide, sodium hydroxide and potassium hydroxide, and mono- and polyhydric alcohols of up to about 30 carbon atoms. Examples of the alcohols include methanol, ethanol, isopropanol, dodecanol, behenyl alcohol, ethylene glycol, monomethylether of ethylene glycol, hexamethylene glycol, glycerol, pentaerythritol, benzyl alcohol, phenylethyl alcohol, aminoethanol, cinnamyl alcohol, allyl alcohol, and the like. Especially useful are the monohydric alcohols having up to about 10 carbon atoms and mixtures of methanol with higher monohydric alcohols.

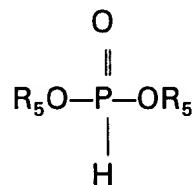
Patents specifically describing techniques for making basic salts of the

above-described sulfonic acids, carboxylic acids, and mixtures of any two or more of these include U.S. Patents 2,501,731; 2,616,905; 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109. The disclosures of these patents are hereby incorporated in this present specification for their disclosures in this regard as well as for their disclosure of specific suitable basic metal salts.

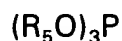
(B) Hydrocarbyl Phosphites

Compositions of the present invention also include (C) a hydrocarbyl phosphite. The phosphite is present in an amount to deliver from about 0.01% to about 0.3%, or from about 0.03% to about 0.25% phosphorus to the final lubricant. Typically the lubricant contains up to about 3% by weight of (B). Generally the lubricants contains from about 0.05% to about 5%, or from about 0.02% to about 2%, or from about 0.1% to about 2%, or from about 0.2% to about 1.5%, or from 0.3% to about 1% by weight of the lubricant.

The phosphite may be represented by the following formulae:



or



wherein each R_5 is independently hydrogen or a hydrocarbyl group, provided at least one R_5 is hydrocarbyl. Preferably each R_5 is independently a hydrogen or hydrocarbyl group having from 1 to about 24, or from 1 to about 18, and or from about 2 to about 8 carbon atoms. Each R_5 may be independently alkyl, alkenyl or aryl. When R_5 is aryl it contains at least 6 carbon atoms; preferably 6 to about 18 carbon atoms. Examples of alkyl or alkenyl groups are propyl, butyl, hexyl, heptyl, octyl, oleyl,

linoleyl, stearyl, etc. Examples of aryl groups are phenyl, naphthyl, heptylphenol, etc. Preferably each R_5 is independently propyl, butyl, pentyl, hexyl, heptyl, oleyl or phenyl, more preferably butyl, oleyl or phenyl and more preferably butyl or oleyl.

The R_5 groups may also comprise a mixture of hydrocarbyl groups derived from commercial alcohols. Examples of preferred monohydric alcohols and alcohol mixtures include commercially available "Alfol" alcohols marketed by Continental Oil Corporation. Alfol 810 is a mixture containing alcohols consisting essentially of straight-chain, primary alcohols having 8 to 10 carbon atoms. Alfol 812 is a mixture comprising mostly C_{12} fatty alcohols. Alfol 1218 is a mixture of synthetic, primary, straight-chain alcohols having from 12 to 18 carbon atoms. Alfol 20+ alcohols are mixtures of 18-28 primary alcohols having mostly, on an alcohol basis, C_{20} alcohols as determined by GLC (gas-liquid-chromatography).

Another group of commercially available alcohol mixtures includes the "Neodol" products available from Shell Chemical Company. For example, Neodol 23 is a mixture of C_{12} and C_{13} alcohols; Neodol 25 is a mixture of C_{12} and C_{15} alcohols; and Neodol 45 is a mixture of C_{14} and C_{15} linear alcohols. Neodol 91 is a mixture of C_9 , C_{10} and C_{11} alcohols.

Phosphites and their preparation are known and many phosphites are available commercially. Particularly useful phosphites are dibutylhydrogen phosphite, trioyleyl phosphite and triphenyl phosphite. Phosphite esters are generally dialkyl hydrogen phosphites.

A number of dialkyl hydrogen phosphites are commercially available, such as lower dialkyl hydrogen phosphites, which are preferred. Lower dialkyl hydrogen phosphites include dimethyl, diethyl, dipropyl, dibutyl, dipentyl and dihexyl hydrogen phosphites. Also mixed alkyl hydrogen phosphites are useful in the present invention. Examples of mixed alkyl hydrogen phosphites include ethyl, butyl; propyl, pentyl; and methyl, pentyl hydrogen phosphites.

In one embodiment, the lubricant includes minor amounts of other phosphorus additives. These additives are present in amounts less than 2%, or less than 1%, or

less than 0.5% by weight. In another embodiment, the phosphite or mixture of phosphites is the sole source of phosphorus added by components of the lubricant.

(C) Friction Modifier

5 In one embodiment, the lubricants include (C) at least one friction modifier. The friction modifier is one which reduces friction. The friction modifier is present in an amount from about 0.01% to about 2%, or from about 0.05% to about 1%, or from about 0.1% to about 0.6% by weight. The friction modifier may be any friction modifier known to those in the art. Examples of friction modifiers include a fatty phosphite, a fatty acid amide, a fatty amine, a borated fatty amine, a borated fatty epoxide, a glycerol ester and a borated glycerol ester. Mixtures of friction modifiers may be used as well.

10 In one embodiment, the friction modifier is fatty acid esters of polyols. The fatty acids are those having from about 8 to about 30, or from about 12 to about 24 carbon atoms. Examples of these fatty acids include stearic acid, oleic acid, tallow acid, etc. The polyols generally has from about 2 to about 8, or from about 3 to about 6 hydroxyl groups and form about 2 to about 18, or from about 3 to about 12, or from 4 to 8 carbon atoms. The polyols include alkylene, such as ethylene or butylene, glycols, erythritol, pentaerythritol, diethyleneglycol, sorbitol, glycerol, etc. A particularly useful fatty ester of a polyols is a glycerol based esters such as glycerol mono-, di- or trioleate.

15 In one embodiment the fatty esters are glycerol esters. The glycerol esters useful in the present invention are glycerol esters of fatty acids, such as fatty acids having from about 8 to about 22 carbon atoms, preferably about 12 to about 20. Examples of fatty acids useful in preparing the esters are oleic, stearic, linoleic acids and the like. The esters may be mono-, di-, or triesters of fatty esters. Glycerol mono-oleate and glycerol tallowate are known commercial materials. It is generally recognized that esters of glycerol are actually mixtures of mono- and diesters. A particularly useful ester is a mixture of mono- and diester containing at least 40% of

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the monoester of glycerol. Preferably, the mixtures of mono- and diesters of glycerol contain from about 40 to about 60% by weight of the monoester. For example, commercial glycerol monoleate contains a mixture of from about 45% to about 55% by weight monoester and from 55% to about 45% of the monoester. Glycerol monoleate in its commercially available mixtures are preferred.

The borated glycerol esters are also useful in the present invention and are prepared by reacting the fatty acid ester of glycerol with boric acid and removal of water. Preferably, the boric acid and the fatty acid ester are reacted such that each boron will react with from 1.5 to about 2.5 hydroxy groups present in the mixture. The reaction may be carried out at a temperature in the range of from about 60°C. to about 135°C. in the absence or presence of any suitable organic solvent such as methanol, benzene, xylene, toluene, or the like.

In another embodiment, the friction modifier (C) may be a fatty amide or amine. The fatty amide or amine have substituent group analogous to the above described fatty acids. Oleylamide and oleylamine are examples of these friction modifiers. The fatty acid amides which are useful in the present invention are generally amides derived from fatty acids having from about 4 to about 28, preferably about 12 to about 22, preferably about 16 to about 20 carbon atoms. A particularly useful fatty acid amide is oleyl amide, linoleyl amide, stearyl amide or tall oil amide, with oleyl amide being preferred. The fatty amines useful as friction modifiers are generally primary, secondary or tertiary amines having alkyl, alkoxy or polyoxyalkene groups. The borated fatty amines are prepared by reacting a borating agent (described above) with a fatty amine (described above). The borated fatty amines are prepared by reacting the amine with the borating agent at about 50°C to about 300°C, preferably about 100°C to about 250°C, and at a ratio of 3:1 to 1:3 equivalents of amine to equivalents of borating agent.

In another embodiment, the friction modifier (C) may be a fatty phosphite. The fatty phosphites include dialkyl hydrogen phosphites having alkyl groups having from about 8 to about 24, preferably about 12 to about 22, more preferably about 16 to

about 20 carbon atoms in each alkyl group. A particularly useful fatty phosphite is a dioleoyl hydrogen phosphite.

In another embodiment, the friction modifier is a borated fatty epoxide. The borated fatty epoxides are generally the reaction product of a boric acid or boron trioxide with at least one epoxide. The epoxide is generally an aliphatic epoxide having at least 8 carbon atoms, more preferably from about 10 to about 20, more preferably 12 to about 20. Examples of useful aliphatic epoxides include heptyl oxide, octyl oxide, stearyl oxide, oleyl oxide and the like. Mixtures of epoxides may also be used, for instance commercial mixtures of epoxides having from 14 to about 16 carbon atoms and 14 to about 18 carbon atoms. The borated fatty epoxides are generally known and are disclosed in Canadian Patent 1,188,704 issued to Davis. This patent is incorporated by reference for its disclosure of borated fatty epoxides and methods for preparing the same.

U.S. Patent 4,792,410, issued to Schwind et al, described friction modifiers and that disclosure is hereby incorporated by reference.

(D) Acylated Amine

The composition may contain an acylated amine. Typically, the acylated amine has a total base number of at least about 30 TBN, or preferably at least about 40 TBN, more preferably at least about 50 TBN. The basic nitrogen compounds generally have a maximum TBN of about 350, preferably about 250. In one embodiment, the acylated amine has a TBN from about 30 to about 200, preferably from about 60 up to about 150, or more preferably from about 70 up to about 100. The TBN is based on neat chemical.

The acylated amine includes reaction products of one or more carboxylic acylating agent and one or more amine, preferably a polyamine. In one embodiment, the acylated amines are prepared by reacting an excess of amine with the carboxylic acylating agent. In one embodiment, greater than one equivalent of amine is reacted with each equivalent of carboxylic group of the acylating agent. The equivalents of the amine is based on the number of nitrogen atoms in the amine.

The equivalent weight of the carboxylic acylating agent is based on the number of carboxylic groups (e.g. COO), such as acids, lower esters, etc. in each acylating agent. In one embodiment, at least about 1.2, preferably at least about 1.4 equivalents of amine are reacted with each equivalent of carboxylic group of the acylating agent. Typically, up to about 8, or preferably up to about 6, or more preferably up to about 4 equivalents of amine are reacted with each equivalent of carboxylic group of the acylating agent.

The acylated amines are prepared from one or more amines and one or more carboxylic acylating agents. The carboxylic acylating agents include fatty acids, isoaliphatic acids, dimer acids, addition dicarboxylic acids, trimer acids, addition tricarboxylic acids, and hydrocarbyl substituted carboxylic acylating agents. In one embodiment, the carboxylic acylating agent is one of the above described unsaturated fatty acids. The fatty acids may also be the saturated analogs of the unsaturated fatty acids.

In another embodiment, the carboxylic acylating agents include isoaliphatic acids. Such acids contain a principal saturated, aliphatic chain typically having from about 14 to about 20 carbon atoms and at least one, but usually no more than about four, pendant acyclic lower alkyl groups. Specific examples of such isoaliphatic acids include 10-methyl-tetradecanoic acid, 3-ethyl-hexadecanoic acid, and 8-methyl-octadecanoic acid. The isoaliphatic acids include branched-chain acids prepared by oligomerization of commercial fatty acids, such as oleic, linoleic and tall oil fatty acids.

The dimer acids include products resulting from the dimerization of unsaturated fatty acids and generally contain an average from about 18 to about 44, or from about 28 to about 40 carbon atoms. Dimer acids are described in U.S. Patents 2,482,760, 2,482,761, 2,731,481, 2,793,219, 2,964,545, 2,978,468, 3,157,681, and 3,256,304, the entire disclosures of which are incorporated herein by reference.

In another embodiment, the carboxylic acylating agents are addition carboxylic acylating agents, which are addition (4 + 2 and 2 + 2) products of an unsaturated fatty

acid, such as tall oil acids and oleic acids, with one or more unsaturated carboxylic reagents, which are described below. These acids are taught in U.S. Patent No. 2,444,328, the disclosure of which is incorporated herein by reference.

In another embodiment, the carboxylic acylating agent is a tricarboxylic acylating agent. Examples of tricarboxylic acylating agents include trimer acylating agents and the reaction product of an unsaturated carboxylic acylating agent (such as unsaturated fatty acids) and an alpha,beta- unsaturated dicarboxylic acylating agent (such as maleic, itaconic, and citraconic acylating agents, preferably maleic acylating agents). These acylating agents generally contain an average from about 18, or about 30, or about 36 to about 66, or to about 60 carbon atoms. The trimer acylating agents are prepared by the trimerization of one or more of the above-described fatty acids. In one embodiment, the tricarboxylic acylating agent is the reaction product of one or more unsaturated carboxylic acylating agent, such as an unsaturated fatty acid or unsaturated alkenyl succinic anhydride and an alpha,beta-unsaturated carboxylic reagent. The unsaturated carboxylic reagents include unsaturated carboxylic acids per se and functional derivatives thereof, such as anhydrides, esters, amides, imides, salts, acyl halides, and nitriles. The unsaturated carboxylic reagent include mono, di, tri or tetracarboxylic reagents. Specific examples of useful monobasic unsaturated carboxylic acids are acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, 2-phenylpropenoic acid, etc. Exemplary polybasic acids include maleic acid, maleic anhydride, fumaric acid, mesaconic acid, itaconic acid and citraconic acid. Generally, the unsaturated carboxylic reagent is maleic anhydride, acid or lower ester, e.g. those containing less than eight carbon atoms. In one embodiment, the unsaturated dicarboxylic acylating agent generally contains an average from about 12 up to about 40, or from about 18 up to about 30 carbon atoms. Examples of these tricarboxylic acylating agents include Empol® 1040 available commercially from Emery Industries, Hystrene® 5460 available commercially from Humko Chemical, and Unidyme® 60 available commercially from Union Camp Corporation.

In another embodiment, the carboxylic acylating agent is a hydrocarbyl

substituted carboxylic acylating agent. The hydrocarbyl substituted carboxylic acylating agents are prepared by a reaction of one or more olefin or polyalkene with one or more of the above described unsaturated carboxylic reagents. The hydrocarbyl group generally contains from about 8 to about 300, or from about 12 up to about 200, or from about 16 up to about 150, or from about 30 to about 100 carbon atoms. In one embodiment, the hydrocarbyl group contains from about 8 up to about 40, or from about 10 up to about 30, or from about 12 up to about 24 carbon atoms. In one embodiment, the hydrocarbyl group may be derived from an olefin. The olefins typically contain from about 3 to about 40, or from about 4 to about 24 carbon atoms. These olefins are preferably alpha-olefins (sometimes referred to as mono-1-olefins or terminal olefins) or isomerized alpha-olefins. Examples of the alpha-olefins include 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1-tetracosene, etc. Commercially available alpha-olefin fractions that can be used include the C₁₅₋₁₈ alpha-olefins, C₁₂₋₁₆ alpha-olefins, C₁₄₋₁₆ alpha-olefins, C₁₄₋₁₈ alpha-olefins, C₁₆₋₁₈ alpha-olefins, C₁₆₋₂₀ alpha-olefins, C₁₈₋₂₄ alpha-olefins, C₂₂₋₂₈ alpha-olefins, etc.

In another embodiment, the hydrocarbyl group is derived from one or more of the above described polyalkenes. In one embodiment, the polyalkenes have a Mn from at least about 1300, or from about 1500, or from about 1700. In one embodiment, the polyalkenes have a Mn from about 1500 up to about 3200, or from about 1500 up to about 2800, or from about 1500 up to about 2400. In a preferred embodiment, the polyalkene has a Mn from about 1700 to about 2400. The polyalkenes also generally have a Mw/Mn from about 1.5 to about 4, or from about 1.8 to about 3.6, or from about 2.0 to about 3.4, or from about 2.5 to about 3.2. The hydrocarbyl substituted carboxylic acylating agents are described in U.S. Patent 3,219,666 and 4,234,435, the disclosures of which is hereby incorporated by reference.

In another embodiment, the acylating agents may be prepared by reacting one or more of the above described polyalkenes with an excess of maleic anhydride to provide substituted succinic acylating agents wherein the number of succinic groups for each equivalent weight of substituent group, i.e., polyalkenyl group, is at least about 1.3, preferably at least about 1.4, or more preferably at least about 1.5. The maximum number will generally not exceed about 4.5, or preferably about 3.5. A suitable range is from about 1.4 up to about 3.5, or from about 1.5 up to about 2.5 succinic groups per equivalent weight of substituent groups.

The carboxylic acylating agents are known in the art and have been described in detail, for example, in the following: U.S. Patents 3,215,707 (Rense); 3,219,666 (Norman et al); 3,231,587 (Rense); 3,912,764 (Palmer); 4,110,349 (Cohen); and 4,234,435 (Meinhardt et al); and U.K. 1,440,219. The disclosures of these patents are hereby incorporated by reference. These patents are incorporated herein by reference for their disclosure of carboxylic acylating agents and methods for making the same.

The above-described carboxylic acylating agents are reacted with amines to form the acylated amines. The amines may be monoamines or polyamines preferably the amine is a polyamine, such as an alkylene polyamine or a condensed amine. Useful amines include those amines disclosed in U.S. Patent 4,234,435 at Col. 21, line 4 to Col. 27, line 50, these passages being incorporated herein by reference.

In one embodiment, the amine is a fatty amine. Fatty amines are those containing from about 8 to about 30, or from about 12 to about 24 carbon atoms. The fatty amines include n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, stearylamine, oleyamine, tallowamine, soyaamine, etc. Also useful fatty amines include commercially available fatty amines such as "Armeen" amines (products available from Akzo Chemicals, Chicago, Illinois), such as Akzo's Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as cocoa, oleyl, tallow, or stearyl groups.

Other useful amines include primary ether amines, such as those represented by the formula, $R_1(OR_2)_x NH_2$ (I), wherein R_1 is a hydrocarbyl group from about 1 to about 150, or from 5 to about 24 carbon atoms, R_2 is a divalent alkylene group having about 2 to about 6 carbon atoms; and x is a number from one to about 150, or from about one to about five, or one. An example of an ether amine is available under the name SURFAM® amines produced and marketed by Mars Chemical Company, Atlanta, Georgia. Etheramines include those identified as SURFAM P14B (decyloxypropylamine), SURFAM P16A (linear C_{16}), and SURFAM P17B (tridecyloxypropylamine). The carbon chain lengths (i.e., C_{14} , etc.) of the SURFAMS described above and used hereinafter are approximate and include the oxygen ether linkage.

In another embodiment, the amine is a tertiary-aliphatic primary amine. Generally, the aliphatic group, and in one embodiment an alkyl group, contains from about 4 to about 30, or from about 6 to about 24, or from about 8 to about 22 carbon atoms. Usually the tertiary alkyl primary amines are monoamines represented by the formula $R_1-C(R_2)_2-NH_2$ (II), wherein R_1 is a hydrocarbyl group containing from 1 to about 28 carbon atoms and R_2 is a divalent hydrocarbylene group, preferably an alkylene group, containing from 1 to about 12 carbon atoms. Such amines are illustrated by tert-butylamine, tert-hexylamine, 1-methyl-1-amino-cyclohexane, tert-octylamine, tert-decylamine, tert-dodecylamine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, tert-tetracosanylamine, and tert-octacosanylamine.

Mixtures of amines are also useful for the purposes of this invention. Illustrative of amine mixtures of this type are "Primene 81R" which is a mixture of C_{11} - C_{14} tertiary alkyl primary amines and "Primene JMT" which is a mixture of C_{18} - C_{22} tertiary alkyl primary amines (both are available from Rohm and Haas Company). The tertiary alkyl primary amines and methods for their preparation are known to those of ordinary skill in the art. The tertiary alkyl primary amine useful for the purposes of this invention and methods for their preparation are described in U.S. Patent 2,945,749, which is hereby incorporated by reference for its teaching in this regard.

In another embodiment, the polyamine is a fatty diamine. The fatty diamines include mono- or dialkyl, symmetrical or asymmetrical ethylenediamines, propanediamines (1,2, or 1,3), and polyamine analogs of the above. Suitable commercial fatty polyamines are Duomeen C (N-coco-1,3-diaminopropane), Duomeen S (N-soya-1,3-diaminopropane), Duomeen T (N-tallow-1,3-diaminopropane), and Duomeen O (N-oleyl-1,3-diaminopropane). "Duomeens" are commercially available from Armak Chemical Co., Chicago, Illinois.

In another embodiment, the polyamines are polyoxyalkylene polyamines, e.g. polyoxyalkylene diamines and polyoxyalkylene triamines, having average molecular weights ranging from about 200 to about 4000, or from about 400 to about 2000. The preferred polyoxyalkylene polyamines include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines. The polyoxyalkylene polyamines are commercially available and may be obtained, for example, from the Texaco Chemical Company, Inc. under the trade name "Jeffamines D-230, D-400, D-1000, D-2000, T-403, etc.". U.S. Patents 3,804,763 and 3,948,800 are expressly incorporated herein by reference for their disclosure of such polyoxyalkylene polyamines and acylated products made therefrom.

In another embodiment, the polyamines are hydroxy-containing polyamines. Hydroxy-containing polyamine analogs of hydroxy monoamines, particularly alkoxyalkylenepolyamines, e.g., N,N'-(dihydroxyethyl)ethylene diamines can also be used. Such polyamines can be made by reacting the above-described alkylene amines with one or more alkylene oxides, such as ethylene, propylene or butylene oxide. Similar alkylene oxide-alkanol amine reaction products may also be used such as the products made by reacting the above described primary, secondary or tertiary alkanol amines with ethylene, propylene or higher epoxide in a 1.1 to 1.2 molar ratio. Reactant ratios and temperatures for carrying out such reactions are known to those skilled in the art. Specific examples of hydroxy-containing polyamines include N-(2-hydroxyethyl)ethylenediamine, N,N'-bis(2-hydroxyethyl)ethylenediamine, 1-(2-hydroxyethyl)piperazine, mono(hydroxypropyl)-substituted tetraethylene-

pentamine, N-(3-hydroxybutyl)tetramethylenediamine, etc. Higher homologs obtained by condensation of the above illustrated hydroxy-containing polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia, while
5 condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water. Mixtures of two or more of any of the above described polyamines are also useful.

In another embodiment, the polyamine is a heterocyclic polyamine. The heterocyclic polyamines include aziridines, azetidines, azolidines, tetra- and dihydro-
10 pyridines, pyrroles, indoles, piperidines, imidazoles, di- and tetrahydroimidazoles, piperazines, isoindoles, purines, morpholines, thiomorpholines, N-aminoalkylmorpholines, N-aminoalkylthiomorpholines, N-aminoalkylpiperazines, N,N'-di-aminoalkylpiperazines, azepines, azocines, azonines, azecines and tetra-, di- and per-
15 hydro derivatives of each of the above and mixtures of two or more of these heterocyclic amines. Preferred heterocyclic amines are the saturated 5- and 6-membered heterocyclic amines containing only nitrogen, oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Piperidine, aminoalkyl substituted piperidines, piperazine, aminoalkyl substituted piperazines, morpholine, aminoalkyl substituted morpholines, pyrrolidine, and aminoalkyl-substituted pyrrolidines, are especially preferred. Usually the
20 aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring. Specific examples of such heterocyclic amines include N-aminopropylmorpholine, N-aminoethylpiperazine, and N,N'-diaminoethylpiperazine. Hydroxy heterocyclic polyamines may be used and include N-(2-hydroxyethyl)cyclohexylamine, 3-hydroxy-cyclopentylamine, parahydroxyaniline, N-hydroxyethylpiperazine, and the like.
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The amine used in preparing the acylated amine may be an alkylenepolyamine. Alkylenepolyamines are represented by the formula $H(R_1)N-(Alkylene-N)_n-(R_1)_2$ (III), wherein each R_1 is independently hydrogen; or an aliphatic or hydroxy-substituted aliphatic group of up to about 30 carbon atoms; n is a number from 1 to about 10, or

from about 2 to about 7, or from about 2 to about 5; and the "Alkylene" group has from 1 to about 10 carbon atoms, or from about 2 to about 6, or from about 2 to about 4. In another embodiment, R₁ is independently a hydrocarbyl group having from one to about eight carbon atoms or hydroxyhydrocarbyl group having from one to about eight carbon atoms, or from one to about four. Such alkylene polyamines include methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, etc. The higher homologs and related heterocyclic amines, such as piperazines and N-amino alkyl-substituted piperazines, are also included. Specific examples of such polyamines are ethylenediamine, triethylenetetramine, tris-(2-aminoethyl)amine, propylenediamine, trimethylenediamine, tripropylenetetramine, triethylenetetraamine, tetraethylenepentamine, hexaethyleneheptamine, pentaethylenehexamine, etc. Higher homologs obtained by condensing two or more of the above-noted alkylene amines are similarly useful as are mixtures of two or more of the aforescribed polyamines.

In one embodiment, the polyamine is an ethylene polyamine. Such polyamines are described in detail under the heading Ethylene Amines in Kirk Othmer's "Encyclopedia of Chemical Technology", 2d Edition, Vol. 7, pages 22-37, Interscience Publishers, New York (1965). Ethylene polyamines are often a complex mixture of polyalkylene polyamines including cyclic condensation products. Other useful types of polyamine mixtures are those resulting from stripping of the above-described polyamine mixtures to leave, as residue, what is often termed "polyamine bottoms". In general, alkylene polyamine bottoms can be characterized as having less than 2%, usually less than 1% (by weight) material boiling below about 200°C. A typical sample of such ethylene polyamine bottoms obtained from the Dow Chemical Company of Freeport, Texas designated "E-100" has a specific gravity at 15.6°C of 1.0168, a percent nitrogen by weight of 33.15 and a viscosity at 40°C of 121 centistokes. Gas chromatography analysis of such a sample contains about 0.93% "Light Ends" (most probably diethylenetriamine), 0.72% triethylenetetraamine, 21.74% tetraethylenepentaamine and 76.61% pentaethylenehexamine and higher analogs.

These alkylenepolyamine bottoms include cyclic condensation products such as piperazine and higher analogs of diethylenetriamine, triethylenetetramine and the like. These alkylenepolyamine bottoms may be reacted solely with the acylating agent or they may be used with other amines, polyamines, or mixtures thereof.

5 Another useful polyamine is a condensation reaction between at least one hydroxy compound with at least one polyamine reactant containing at least one primary or secondary amino group. The hydroxy compounds are preferably polyhydric alcohols and amines. The polyhydric alcohols are described below. In one embodiment, the hydroxy compounds are polyhydric amines. Polyhydric amines include any of the above-described monoamines reacted with an alkylene oxide (e.g.,
10 ethylene oxide, propylene oxide, butylene oxide, etc.) having from two to about 20 carbon atoms, or from two to about four. Examples of polyhydric amines include diethanolamine, triethanolamine, tri-(hydroxypropyl)amine, tris-(hydroxymethyl)amino methane, 2-amino-2-methyl-1,3-propanediol, N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine, and N,N,N',N'-tetrakis (2-hydroxyethyl) ethylenediamine, preferably
15 tris(hydroxymethyl) aminomethane (THAM).

Polyamines which may react with the polyhydric alcohol or amine to form the condensation products or condensed amines, are described above. Preferred polyamines include triethylenetetramine (TETA), tetraethylenepentamine (TEPA), penta-
20 ethylenehexamine (PEHA), and mixtures of polyamines such as the above-described "amine bottoms". The condensation reaction of the polyamine reactant with the hydroxy compound is conducted at an elevated temperature, usually from about 60°C to about 265°C, or from about 220°C to about 250°C in the presence of an acid catalyst.

25 The amine condensates and methods of making the same are described in PCT publication WO86/05501 and U.S. Patent 5,230,714 (Steckel) which are incorporated by reference for its disclosure to the condensates and methods of making. A particularly useful amine condensate is prepared from HPA Taft Amines (amine bottoms available commercially from Union Carbide Co. with typically 34.1% by weight

nitrogen and a nitrogen distribution of 12.3% by weight primary amine, 14.4% by weight secondary amine and 7.4% by weight tertiary amine), and tris(hydroxymethyl)-aminomethane (THAM).

Acylated amines and methods for preparing the same are described in U.S. Patents 3,219,666; 4,234,435; 4,952,328; 4,938,881; 4,957,649; and 4,904,401. The disclosures of acylated nitrogen dispersants and other dispersants contained in those patents are hereby incorporated by reference.

The following Examples relate to basic nitrogen containing compounds and methods of preparing the same.

Example N-1

A polyisobutenyl ($M_n = 850$) succinic anhydride having an acid number of 113 (corresponding to an equivalent weight of 500). To a mixture of 500 grams (1 equivalent) of this polyisobutenyl succinic anhydride and 160 grams of toluene there is added at room temperature 55.5 grams (1.5 equivalents) of an ethylene amine mixture having a composition corresponding to that of triethylenetetramine. The addition is made portionwise throughout a period of 15 minutes. The mixture then is heated and a water-toluene azeotrope distilled from the mixture. When no more water would distill the mixture is heated to 150°C at reduced pressure to remove the toluene. The residue is diluted with 350 grams of mineral oil. The resulting product has a nitrogen content of 1.9%.

Example N-2

The procedure of Example N-1 is repeated using 55.0 grams (1.5 equivalents) of triethylenetetramine as the amine reactant. The resulting product has a nitrogen content of 2.9%.

Example N-3

A mixture of 86.4 grams of an alkylenepolyamine mixture, comprising 80% of ethylene polyamine bottoms from Union Carbide and 20% of a commercial mixture of ethylenepolyamines corresponding in empirical formula to diethylenetriamine, and 390 grams of 100 neutral mineral oil is heated to 100°C under nitrogen. To this mixture is added 800 grams of polybutenyl ($n = 1000$) substituted succinic anhydride and 200 grams of 100 neutral mineral oil. The reaction mixture is heated to 290-300°F and the temperature is maintained for one hour, with submerged nitrogen blowing. The reaction product is then filtered and the filtrate is the desired product. The desired product is a 40% oil mixture having 2% nitrogen, and a 45 TBN.

Example N-4

To a mixture of 140 grams of toluene and 400 grams (0.78 equivalent) of a polyisobutenyl ($M_n = 850$) succinic anhydride, having an acid number of 109, there is added at room temperature 63.6 grams (1.55 equivalents) of an ethyleneamine mixture having an average composition corresponding to that of tetraethylenepentamine and available from Union Carbide under the trade name "Polyamine H." The mixture is heated to distill the water-toluene azeotrope and then to 150°C. at reduced pressure to remove the remaining toluene. The residual polyamide has a nitrogen content of 4.7%.

Example N-5

Following the procedure of Example N-3, 116 grams of the polyamine mixture of Example N-3 and 388 grams of 100 neutral mineral oil are reacted with 800 grams of the polybutenyl succinic anhydride of Example N-3 and 200 grams of a 100 neutral mineral oil. The desired product is a 40% oil mixture having 2.5% nitrogen and a 70 TBN.

Example N-6

The procedure of Example N-1 is repeated using 46 grams (1.5 equivalents) of ethylene diamine as the amine reactant. The product which resulted has a nitrogen content of 1.5%.

Example N-7

A reaction vessel is charged with 1000 grams of the polybutenyl succinic anhydride of Example N-3 and 400 grams of 100 neutral mineral oil. The mixture is heated to 88°C where 152 grams of a polyamine prepared from: 1299 grams of HPA Taft Amines (amine bottoms available commercially from Union Carbide Co. with typically 34.1% by weight nitrogen and a nitrogen distribution of 12.3% by weight primary amine, 14.4% by weight secondary amine and 7.4% by weight tertiary amine), 727 grams of 40% aqueous tris(hydroxymethyl)aminomethane (THAM), and 23 grams of 85% H₃PO₄ which are heated to 120°C over 0.6 hour, then are heated to 150°C over 1.25 hour, then to 235°C over 1 hour, then the temperature is maintained at 230-235°C for 5 hours, then heated to 240°C over 0.75 hour, and then held at 240-245°C for 5 hours, followed by filtration through diatomaceous earth. The mixture is heated to 152°C over 5.5 hours. At temperature, the reaction mixture is blown subsurface with nitrogen until the percent water is a maximum of 0.3. Diluent oil (342 grams of 100 neutral mineral oil) is added to the reaction mixture and the reaction mixture is filtered through diatomaceous earth. The filtrate is the desired product. The desired product is a 40% oil mixture having 2.1% nitrogen and a 48 TBN.

Example N-8

An acid producing compound is prepared by heating chloromaleic anhydride (1 equivalent) and 1 equivalent of a chlorinated polyisobutene having a chlorine content of 4% and a molecular weight of 2500 at 150 -200°C. The product of the reaction is then mixed with tetraethylenepentamine (2.5 equivalents) at 50°C and the mixture is heated at 180 -210°C to form an acylated polyamine.

The lubricants may contain other additives such as dyes, cold flow modifiers, auxiliary antiwear agents such as metal dithiophosphates (such as zinc dithiophosphates), phosphate esters or salts, such as tricresylphosphate or 2-ethylhexyl phosphates and salts thereof, sulfurized C₂₋₁₂ olefins, sulfurized fatty acids or oils, etc.

In one embodiment, the lubricants consist essentially of (A) and (B). In another embodiment, the lubricant consists essentially of (A), (B) and (C). In these embodiment, the components provide durability in the Mack MT-1 transmission test and have improved antiwear and thermal stability properties.

The following examples relate to the lubricants which contain at least a basic metal salt and a hydrocarbyl phosphite. Unless otherwise indicated, in the following examples as well as elsewhere in the specification and claims, temperature is in degrees Celsius, parts and percentages are by weight and pressures are atmospheric.

Example 1

A lubricant is prepared by blending 0.75% of di-2-ethylhexyl hydrogen phosphite and 0.7% of a calcium benzene sulfonate, having 53% 100 neutral mineral oil, a total base number or 41, a metal ratio of 12, and 2.5% of calcium methylene coupled heptylphenate having 2.2% calcium and a total base number of 65 into a base stock prepared from combining 73%v of 750 neutral mineral oil and 27%v of 150 bright stock.

Example 2

A lubricant is prepared as described in Example 1 except that 1.5% of dioleoyl phosphite is used in place of di-2-ethylhexyl phosphite.

Example 3

5 A lubricant is prepared as described in Example 1 except that 0.6% of dibutyl phosphite is used in place of di-2-ethylhexyl phosphite.

Example 4-6

10 A lubricant is prepared as described in Example 1-3 except that 0.6% of a magnesium benzene sulfonate having 42% 100 neutral mineral oil, 9.4% magnesium, a metal ratio of 14.7, a total base number of 400 and 5% of polyisobutylene (Mn = 980) succinic anhydride is used as the only basic salt.

15 While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.